

References referred to in

**METHOD FOR THE PRODUCTION OF HIGH YIELD CHEMICAL PULP FROM  
SOFTWOOD**

**Enclosed;**

Alkaline Pulping, Vol 5, Pulp and Paper Manufacture Series, TAPPI, 1989.Fig.126, p 1  
and p 159

E.A., Backlund “ Extended delignification...”, TAPPI Journal , Nov.,1984; pp.62-65.

## METHOD FOR THE PRODUCTION OF HIGH YIELD CHEMICAL PULP FROM SOFTWOOD

The present invention relates to a method for the production of high yield chemical pulp from softwood by the addition of a delignification catalyst to the wood chips prior to pulping and using alkaline pulping liquors comprising boron compounds at white liquor sulfidity levels below about 25 %.

### Background to the invention

Sulfate or kraft pulp with a lignin content corresponding to a Kappa number of from about 40 to about 125 is conventionally used for the production of unbleached linerboard, kraftliner and sack paper products. Linerboard and sack pulp manufactured this way has good strength properties at relatively high yields (55-65%). Softwood pulps produced in this kappa range may also be further treated by oxygen and alkali to increase brightness or be used as an intermediate step in producing fully bleached pulps from softwood.

The dry weight of washed fibers, which are recovered after pulping, is generally reported as percentage of the weight of dry lignocellulosic material, which was charged to the digestion process. This percentage is termed "yield." Any decrease in yield caused by loss of lignocellulosic materials is undesirable in papermaking. The cooking yield for preparation of bleached softwood pulp qualities is in the order of 45-48 % on wood. High yield pulping in conjunction with alkaline pulping is hereinafter referred to when the yield on wood is higher than about 50 % on wood.

Kraftliner is a board paper with a grammage weight basis in the range of 100 – 450 g/m and traditionally manufactured from unbleached kraft pulp. The linerboard comprises a basic layer to obtain the desired strength properties and a surface layer based on further refined pulp and/or bleached kraft pulp. Linerboard is also prepared in three layers, wherein recycled fibers may be used in the middle layer. If the middle layer is based solely on recycled fibers the board material is referred to as testliner. Testliner qualities may also have recycled fibers in the top layer.

Prime quality kraftliner is manufactured from clean, unbleached softwood pulp. The proportions between spruce, pine and other softwoods may vary but pine is the predominant raw material the Northern hemisphere. Birch or other hardwood pulps can be

mixed into the raw liner pulp, however strength properties may suffer should the proportion of hardwood exceed about 20 %. Birch or other hardwood pulps are advantageously used in the top layer of a multi-ply linerboard.

5 Linerboard pulps are normally produced by the traditional sulfate or kraft process wherein the lignocellulosic material is cooked with an aqueous mixture of sodium hydroxide and sodium sulfide. This aqueous liquor is named white liquor. The content of sulphide in the white liquor, commonly termed sulfidity, is calculated as  $\text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{NaOH})$ , in % based on molar equivalents. Preparation of high yields pulps for linerboard or sack paper production using pulping liquor sulfidity levels below about 25 % are sparsely, if at all  
10 reported. The cooking is carried out in a digester at a temperature and time relationship commonly related to as the H-factor. The H-factor allows a presentation of the cooking time and temperature as a single variable. The H-factor needed in a standard kraft softwood cook for preparation of a kraftliner pulp is in the order of 700-1200.

15 While the kraft pulping process has several advantages that account for its widespread use, there are also disadvantages, including odor emissions, sulfur chemicals inventory problems and the need for a selective sulfur chemicals purge system. To date however, alternative-pulping technologies generally cannot match the overall economics and pulp strength of the kraft process.

20 An alternative to the use of sulfur based pulping accelerators is described by Holton in U.S. Pat. No. 4,012,280 in which the addition and use of quinone compounds such as naphthoquinone, anthraquinone (AQ), phenanthrenequinone, anthrone and their ring substituted derivatives are claimed as accelerators in the wood pulping process. AQ is used at <0.1% levels (on dry wood) to improve the rate of delignification and lower environmental impact by increasing pulping rates and product yield. AQ can be used in  
25 cooking liquor with alkali hydroxide only (soda/AQ) or together with hydroxide and sulfide in a kraft process; in the latter case, the sulfur content of the liquor can be reduced and less odorous emissions occur.

30 While AQ is effective as a catalyst for improving the rate of delignification and lowering environmental impacts, the commercial use of AQ is still limited to pulping hardwood and nonwood due to inferior pulp strength properties of softwood pulps. Furthermore, as certain processes in the modern softwood kraft mill traditionally uses low cost sulfur

chemicals for acidulation purposes it is difficult to decrease, let alone to remove, sulfur from the chemicals recovery system in the softwood kraft mill. Sulfur free chemicals for use in acidulation stages or new process designs are called for in order to enable a decrease in overall mill sulfidity.

- 5 The management of sulfur chemicals in the modern kraft mill has become much more complicated along with stricter environmental legislation and increased recycle of mill effluents. While sulfur management problems are present in all modern kraft mills, specific sulfur inventory build up and problems arises in sack and kraftliner pulp mills using softwood wood raw material. The reason for this is that the natural sulfur chemicals purge  
10 in bleached kraft mills through bleach plant effluents is not an option for production of unbleached pulp qualities.

The tall oil plant is the dominant user and a major input of fresh sulfur chemicals in the unbleached softwood kraft mill. Tall oil is an important by-product from digestion of softwoods originating from the extractives in the wood. These extractives reacts with the  
15 alkaline pulping liquor to form tall oil soaps. The recovered tall oil soap is normally acidulated with sulfuric acid to form crude tall oil. Apart from crude tall oil a waste brine stream is formed comprising sodium and sulfur compounds. This stream is recycled to the kraft mill chemicals recovery. Typical sulfuric acid charge to a tall oil plant in kraftliner mill is in the order of 200 kg as concentrated  $H_2SO_4$  per ton of tall oil product. The tall oil  
20 yield for Scandinavian pine is in the order of 40 kg crude tall oil per ton of pulp corresponding to a sulfur intake in the order of 7000 ton sulfur per year for a 500 000 ton/year kraftliner mill. It is therefore difficult to operate kraftliner mills at liquor sulfidity levels below 35 %, let alone at 25 % sulfidity or lower. Sulfur has to be purged from the mill to minimize odorous emissions and to balance sulfur input to the mill. Sulfur purge  
25 through removal of recovery boiler ESP ash is not economically attractive as sodium value is lost from the mill chemicals recovery cycle.

The problem of operating sack and kraftliner softwood pulp mills at low white liquor sulfidity is therefore twofold.

- 30 Firstly, with the introduction of more stringent environmental controls on the emission of air and water pollutants, sulfur losses has to be decreased from all unit operations including the recovery boiler, evaporators and lime kilns. These reduced losses have a drastic impact

on the make-up sodium and sulfur requirements in the kraft pulping process, which balance these losses.

Secondly, the sulfides are excellent pulping catalysts and a decrease in mill sulfidity to levels below about 25 % in the white liquor has a negative impact on key kraft pulp strength properties. While the addition of AQ to the white liquor counteract this negative effect, particularly at lower sulfidity, prior art application of AQ cannot match the efficiency and economics of sulfides used in the manufacturing of high yield chemical pulp from softwood.

Thus, for high yield softwood kraft mills that wishes to operate at a low white liquor sulfidity, a solution to the sulfur management is needed which must involve not only a route for managing and/or lowering of the sulfur intake to the mill but must also provide a pulping scheme that permits operation at lower liquor sulfidity while not sacrificing pulp product quality.

The main object of the present invention is thus to provide a method for operating a high yield softwood kraft pulp mill using alkaline pulping liquors with a sulfidity below about 25 %. Another object is to provide a pulping process with a sufficient rate of delignification and selectivity in order to produce a softwood pulp in a higher yield and at a quality at least on a par with a kraft pulping alternative. A further object is to provide a process which has a lower emission of odorous pollutants. Additional objects will appear hereinafter.

### **Summary of the invention**

The present invention relates to a novel method for the production of high yield chemical pulp from softwood in a pulp mill by the application of a delignification catalyst in an wood impregnation step and using alkaline pulping liquors comprising boron compounds at a white liquor sulfidity level below about 25 % such method practiced along with a controlled sulfur chemicals management in the pulp mill. Specifically, the novel pulping process comprises a separate impregnation step wherein softwood lignocellulosic material is contacted with an aqueous solution comprising a quinone delignification catalyst the treatment taking place at a maximum temperature of 150 degree C for a period of 1 to 120 minutes and at a pH value below about 7. The neutral or acidic impregnation step is optionally followed by extraction of excess impregnation liquor. After impregnation the

chips are cooked in accordance with common practice using batch or continuous digesters using an alkaline cooking liquor with a sulfidity level lower than about 25 %. Besides alkali the cooking liquor comprises dissolved boron compounds which presence have been shown to increase pulping yield. In addition to the yield advantage, boron compounds are well known as autocausticizing agents forming effective alkali without causticizing in the chemicals recovery cycle of a pulp mill. In order to accomplish the lower white liquor sulfidity relative to a kraft process, the method of the invention furthermore comprises at least one of decreasing the recovery of crude tall oil and using acidic compounds substantially free from sulfur for acidulation of tall oil soap. After digestion a softwood pulp is obtained in a yield range from about 50 to 70 % and at a yield level higher than for a kraft reference pulp using the same H factor and charge of alkali. The pulp product of the present invention may advantageously be used in linerboard or sack paper products.

### Detailed description of the invention

It has been discovered that a high yield chemical pulp with excellent physical properties can be produced from softwood using alkaline pulping liquors comprising boron compounds at a sulfidity level of 25 % or lower. The content of boron compounds in the cooking liquor should be within a range corresponding to a molar ratio of sodium to boron of from about 2:1 to 10:1 more preferably from about 2.1 to about 4:1. Too much boron will negatively impact the load on chemicals recovery and evaporation. Too little boron will not provide a yield advantage. In a pulp mill operating in accordance with the method of the present invention the traditional use of sulfuric acid for tall oil recovery and recycle of sulfurous tall oil brine is eliminated by one of i) burning the tall oil soap directly in a recovery furnace and ii) using acids free from sulfur for tall oil soap acidulation. The new process is thus providing a new innovative pulping schedule combined with an appropriate sulfur chemicals management in the mill.

In more detail the method of the present invention as practiced in high yield softwood mill comprises the steps of;

a) contacting softwood chips with an aqueous impregnation solution comprising a quinone compound in an impregnation zone of a closed vessel at a temperature in the range from about 100 C to about 150 C , for a time period of 1 to 120 minutes and at a pH level below about 7.

b) charging an alkaline cooking liquor to softwood chips recovered directly or indirectly from step a), said cooking liquor comprising boron compounds and having a sulfidity level below about 25 %.

c) cooking impregnated softwood chips in the presence of said alkaline cooking liquor in a digester to obtain a brown pulp product in a yield ranging from 50 – 70 %.

d) extracting cellulose spent liquor comprising tall oil soap from step c)

e) removing a major portion of tall oil soap from cellulose spent liquor and concentrating spent liquor in evaporators to provide a stream of concentrated spent black liquor

f) transferring spent black liquor from step e) to a chemicals recovery plant

10 In order to operate the mill at low sulfidity the tall oil soap present in extracted cellulose spent liquor of step d) is further treated by at least one of;

i) acidulating tall oil soap with an acidic compound substantially free from sulfur compounds and,

15 ii) burning tall oil soap in a combustion plant capable of accommodating alkali metal containing fuels.

20 Size reduction of softwood material to chips in step a) is performed in accordance with common practice in chemical pulp mills. While not a critical factor, the thickness of chips should not exceed about 5 mm. The present invention is applicable using all kinds of softwood feed including mixtures of softwoods. Exemplary softwoods include spruce, fir, pine, cedar, juniper and hemlock.

25 Pre-steaming of the chips prior to pulping is commonly practiced to remove entrapped air. During steaming a minor portion of the wood material is lost by the decomposition of organic material and liberation of inorganic compounds in the wood. The steaming condensate thus comprises acetic acid from de-acetylation of the wood and sulfur compounds entering with the wood. The steaming condensate is either separated from the chips and discharged or it follows the wood chips into the pre-impregnation stage. Mechanical decompression of the chips may be used to increase the active surface area of the chips prior to impregnation.

The impregnation zone in the impregnation step a) can be contained in a separate pre-impregnation vessel or constitute the upper part of a continuous digester. In order to obtain the desired liquor to wood ratio in the impregnation zone, spent impregnation liquor can be recycled to the impregnation zone or discharged from the digester or impregnation vessel.

5 The liquor to wood ratio during impregnation is normally in the range from 2:1 to 5:1. The softwood chips are submerged in the aqueous solution during impregnation and subjected to at least one zone where the average pH value is lower than about 7, preferably lower than about 5 and yet more preferable at a pH value in the range of 5 to 2. The desired pH range is at least partly obtained by the dissolution of acidic compounds in situ from the  
10 hydrolysis and thermal decomposition of the softwood material, primarily lignin and glucomannan. Furthermore, a low pH value in the aqueous impregnation solution may promote mass transfer of quinone catalyst into the chips porous structure.

Depending on conditions and wood source, the dissolution of wood substances in the impregnation step a) is accompanied with a yield loss in the order of about 1 to 10 % on  
15 wood. This yield loss is desirable and tends to increase the rate of delignification, selectivity and pulping yield in the following pulping stage. Temperature and time conditions are therefore selected in the impregnation stage to effect a yield (calculated on dry wood) over the impregnation stage a) of from about 90 % to about 99 %, such conditions more preferably set to effect a yield in the range of from about 2 % to 5 %. The  
20 specific conditions will vary with wood source and appropriate conditions should be established by laboratory or mill scale studies. The temperature during impregnation ranges from about 100 C to about 150 C. The retention time ranges from about 1 to about 120 minutes. Indirect heat transfer with steam to impregnation liquor or direct injection of steam in to the wood chips slurry provides thermal energy for controlling the temperature  
25 in the impregnation stage.

The quinone catalyst used in step a) is selected from the group consisting of naphthoquinone, anthraquinone, anthrone, phenanthrenequinone, octa- dimethyl anthraquinone and derivatives and salts thereof and is charged to be present during  
30 impregnation in a quantity of from 0,01 to 0,5 % by weight calculated as active substance on dry wood.

A mechanical dewatering or compression step for removing excess impregnation liquor may be installed after impregnation, but prior to the alkaline cooking step c). An inverted



top separator located within or outside the digester may also accomplish removal of excess impregnation liquor. Such separators are commonly used in continuous digesters for separation of chips and transport liquor. (Alkaline Pulping, Vol 5, Pulp and Paper Manufacture Series, TAPPI, 1989. Fig. 126, page 159 and E.A., Backlund " Extended delignification...", TAPPI Journal , Nov.,1984; pp.62-65.)

The alkaline cooking liquor used in step b) is mainly composed of dissolved sodium, potassium, sulfur and boron compounds. In order to decrease emission of odorous substances and lowering the corrosion in mill equipment, the content of sulfide should not exceed a white liquor sulfidity of 25 %. Preferably the sulfidity of the cooking liquor should be lower than 15 % and yet more preferable lower than about 10 %. It has been discovered that there is a synergistic effect of the acidic application of catalyst and the presence of boron compounds in the pulping liquor on the pulping yield. The boron compounds, present in the cooking liquor, predominantly as borate ions, should be present in a concentration corresponding to a molar ratio of sodium to boron from about 2:1 to 10:1 and yet more preferable in the range of from about 2:1 to about 4:1. The borate ions referred to inhere are predominantly in the form of tetrahydroxy borate ions ( $\text{B(OH)}_4^-$ ), polyborate ions and metaborate ions ( $\text{BO}_2^-$ ), such ions formed upon dissolution of boron containing smelts in an aqueous solution. The addition of make up boron can be made in various locations in the mill including borax addition to the liquor cycle or addition of boric acid for acidulation purpose in the tall oil plant. In a preferred embodiment the alkaline cooking liquor in step b) is composed of a mixture including dissolved alkali metaborate ( $\text{NaBO}_2$ ) and alkali carbonate which substances, or corresponding ions, are present in a combined concentration which is higher than the combined concentration of other dissolved compounds in the cooking liquor. In addition to the yield advantage, alkali metal borates are known to have autocausticizing properties and the limekiln and causticizing department of the mill will be offloaded.

The design of the cooking stage c) is not critical to the present invention and batch as well as continuous digesters can be used. The softwood chips are cooked in accordance with current practice in the art of delignification using a H-factor sufficient to obtain a yield in the range of 50 - 70 %.

In order to minimize the recycle of sulfurous compounds to the mill liquor cycle and thus enable operation at cooking liquor sulfidity below 25 %, the sulfuric acid traditionally used

for acidulation of tall oil soap may partly or fully be replaced by the addition of carbon dioxide in one or more steps to the tall oil soap or during soap skimming. Other chemicals with the capability of liberating the alkali base from the tall oil soap may also be used to replace sulfuric acid in the tall oil plant. Such chemicals include carbon dioxide, carbonic acid, boric acid, acetic acid, hydrochloric acid, nitric acid, oxalic acid, formic acid, acetic acid and boron trifluoride. Weaker acids such as carbon dioxide treatment at atmospheric pressure cannot provide enough acidity for complete acidulation of the tall oil soap and an intermediate and partly acidified tall oil soap product could be recovered. Such intermediate product can be burned as a fuel in the mill or be further upgraded to crude tall oil preferably by the use of substantially sulfur free chemicals. Depending on the content of sulfurous compounds, streams of waste brine from tall oil soap treatments can either be recycled to the mill liquor cycle or be discharged to secondary treatment.

Alternatives to the recovery of crude tall oil is to remove and export the tall oil soap as such, or to burn the soap directly or indirectly in a recovery boiler or in a separate combustion or gasification unit capable of accommodating fuels comprising sodium.

Lowering the recovery of tall oil can be accomplished in different ways in a softwood pulp mill. The drastic lowering or termination of tall oil soap collection, however, may have serious impact on the operability of mill evaporators, recovery boiler operation safety and pulp manufacturing capacity and is therefore normally avoided.

Employment of the pulps produced by the novel method described herein for linerboard manufacturing results in linerboard strength properties (burst, density, compressive strength) at least on a par with that measured in linerboard employing conventional kraft pulp of the same residual lignin content. A multi-ply white top linerboard product can advantageously be manufactured from combining the high yield softwood pulp prepared in accordance with the method of the present invention with a bleached hardwood pulp either imported to the mill or produced separately from the high yield softwood pulp. Pulp for bleaching can be produced in a separate pulping sequence or in a separate digester system using low sulfidity pulping liquors for digestion. For example, a bleached top layer pulp for a multi-ply linerboard product may be prepared from hardwood using pulping liquor with a sulfidity lower than about 25 % and wherein a quinone delignification catalyst is added directly to the low sulfidity pulping liquor.

If it is desired to obtain a higher brightness of the brown softwood pulp prepared in accordance with the present invention, an oxygen containing gas may be added to a digester, to a digester blowline, to a refiner or to a brown stock washer. Such oxygen reacts with chromophores in the pulp and increases its brightness.

- 5 In order to clearly demonstrate the benefits of the method of the present invention an example is given below summarizing laboratory experiments wherein linerboard pulps were prepared in accordance with the present invention for comparison with a kraft reference linerboard pulp.

### Example

- 10 A comparison of yield and pulp physical properties was made between linerboard quality pulps prepared in accordance with the present invention (called NovaFiber pulps) and a kraft softwood pulp reference. The pulping conditions utilized are set forth in Table 1 below. The NovaFiber pulping sequence was preceded by an acidic impregnation step wherein the wood chips were subjected to treatment with an aqueous solution comprising  
15 anthraquinone (AQ). The charge of AQ was 0.2 % calculated on dry wood. The temperature in the impregnation stage was set at 135 C and the total time at this temperature was 30 min. The pH in the impregnation liquid was allowed to drop to about 3. All pulping runs were carried out in uniform size laboratory digesters. In each run, 1,000 grams of O.D. (oven dry) soft wood (Norwegian spruce) chips passing through a 20 mm  
20 diameter screen and retained on a 7 mm screen, were charged into the laboratory digester.

- Cooking liquor containing hydroxide and sulfide corresponding to a sulfidity of 40 % was used for the kraft reference cooks. Sodium hydroxide and dissolved ( $\text{NaBO}_2$ ) sodium metaborate was used as cooking liquor in the NovaFiber cooks. The molar ratio of sodium to boron in the cooking liquor was 4:1. Constant pulping conditions were adopted for each  
25 run and were as follows: liquor-to-wood ratio 4:1; time period to rise to cooking temperature 15 minutes; cooking temperature from 160 to 166 C; time period at cooking temperature from 109 to 232 min. The H factor was calculated including impregnation time and run up time. At the end of each cooking cycle the pulps were recovered and subsequently washed with ambient temperature water, until substantially free of chemicals.  
30 After washing, the pulps were defiberized in a laboratory refiner before screening and

determination of yield except the lower kappa number pulp NovaFiber 63, as the fibers in this pulp were sufficiently liberated after the cook.

The cooks were allowed to proceed until a certain kappa number range (lignin content) was obtained or, alternatively, until a certain and comparable yield was obtained. The results are shown in Table 1.

Table 1.

Pulp	EA charge %	Cooking Temp °C	Cooking time, min	H factor	Kappa no	Yield % on wood
NovaFiber 63	17.6	160	232	1550	63.3	56.2
NovaFiber 86 (low temp)	16	160	180	1200	85.6	59.9
NovaFiber 88 (high temp)	16	166	109	1200	88.2	62.1
Kraft reference (spruce)	16	160	109	730	86.9	57.7

An important conclusion that can be drawn from these results is that the NovaFiber pulps can be produced in higher yields at a higher cooking temperature and at a constant H factor. This result is quite surprising and can only be explained by the use of the acidic impregnation step combined with the boron containing cooking liquor.

As is apparent from the foregoing specification, the present invention may be embodied in various alterations and modifications. It is to be understood that the foregoing description is intended to be merely illustrative and is not to be construed or interpreted as being restrictive or otherwise limiting of the present invention, except as set forth in the hereto appended claims.